

PATENT SPECIFICATION

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(54) PROCESS FOR THE PREPARATION OF POLYETHYLENE TEREPHTHALATE

(71) We, M & T CHEMICALS INC., a corporation organised and existing under the laws of the State of Delaware, United States of America, with executive offices at 100 Park Avenue, New York, New York 10017, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

Polyethylene terephthalate is ordinarily prepared commercially by a two step ester exchange reaction between dimethyl terephthalate and ethylene glycol. The first step of this reaction is an ester interchange reaction between ethylene glycol and dimethyl terephthalate to form bis(β -hydroxyethyl) terephthalate and methanol. The second step involves polymerization of the bis(β -hydroxyethyl) terephthalate with the elimination of ethylene glycol which is volatilized and removed.

The object of this invention is to provide a process for the rapid preparation of polyethylene terephthalate directly from terephthalic acid and ethylene glycol.

The invention provides a process for preparing polyethylene terephthalate, which comprises forming a condensate by heating a mixture of terephthalic acid and ethylene glycol to a temperature of at least 260°C under superatmospheric pressure and thereafter polymerizing said condensate by heating it to a temperature of at least 260°C under subatmospheric pressure in the presence of antimony pentoxide as a catalyst.

When the antimony pentoxide catalyst is present in the initial reaction mixture subjected to the condensation reaction, this reaction, the polymerization of the resulting product and subsequent formation of the polymer into fibre or film can be carried out continuously.

Antimony pentoxide is soluble in hot ethylene glycol in an amount sufficient for it to be effective as a catalyst, i.e. up to 1% based upon the weight of terephthalic acid.

[Price 25p]

When terephthalic acid is reacted with ethylene glycol under superatmospheric pressure at a temperature of 260°C or more an esterification product having the desired characteristics for the subsequent polymerization reaction is obtained. Since the antimony pentoxide catalyst is hydrolytically stable, it may be added prior to the reaction of ethylene glycol with terephthalic acid.

The initial condensation reaction is thus integrated with the subsequent polymerization, which is preferably carried out at a higher temperature, and no ethylene glycol terephthalate esters need actually be separated or purified. The integration of the two steps renders it important to use terephthalic acid of high purity.

The process according to the invention is preferably carried out by introducing into an autoclave, wherein the reactants can be agitated and water can be removed from the reaction mixture, a mixture of 1 to 7 moles of ethylene glycol per mole of high purified terephthalic acid and a catalytic amount of antimony pentoxide. Air is then removed, for example by purging with nitrogen or another oxygen-free inert gas and before heating to reaction temperature, an inert oxygen-free gas, preferably nitrogen, is introduced into the autoclave at a superatmospheric pressure of up to 150 pounds per square inch. The mixture of glycol, terephthalic acid and catalyst is then heated to a temperature which may vary from 260°C to 285°C. The preferred pressure is 50 pounds per square inch.

The molar ratio of ethylene glycol to terephthalic acid may range from 1:1 to 15:1. For any given temperature, a longer reaction period is usually advisable when operating with a lower proportion of glycol. It is usually more economical to operate within the molar ratio of 1:1 to 7:1 of ethylene glycol to terephthalic acid. The by-products, water and some ethylene glycol, are removed as the reaction proceeds. The removal of water may be continuous or intermittent. The water may be removed from

the esterification reaction mixture through a side-arm condenser and receiver both maintained under the pressure of the reaction, e.g. 50 pounds per square inch.

- 5 During the second polymerization step, the pressure in the autoclave is reduced and ethylene glycol is removed until a polymer of the desired molecular weight is obtained. The temperature may be raised during poly-
10 merization to increase the polymerization rate and to maintain a molten reaction mixture. Temperatures in the range of 260°C to 300°C are suitable with a pressure below 10 millimeters of mercury. It is preferable
15 to conduct the polymerization at a temperature of about 280°C and under a vacuum of less than 5 millimeters of mercury. For optimum results the polymerization reaction is carried out at a pressure below 1 milli-
20 meter of mercury, and usually at or below 0.5 millimeters of mercury. This reduced pressure is necessary to remove free ethylene glycol formed during the polymerization reaction. Ethylene glycol is volatilized under
25 these conditions and is removed from the system. In general, the lower the temperature the longer the time required to effect complete polymerization.

- In a continuous process, the solid product
30 of the direct esterification will produce an acceptable fibre and film-forming polyester of light colour when heated at 760 millimetres of mercury to 100 millimetres of mercury to a temperature sufficient to distil
35 off unreacted diol. The temperature at which the unreacted diol is distilled off is not critical but should provide for as rapid removal of the diol as can be accomplished without excess foaming and entrainment of foam in
40 the vapour. It is preferred to heat and gradually reduce the pressure. It is advantageous to employ an inert oxygen-free gas sweep, for example by bubbling nitrogen through the mixture while the last portions
45 of unreacted diol are being removed. The mixture becomes increasingly viscous so that the viscous mixture should be vigorously agitated to aid in the removal of the diol split out. It is also advantageous to heat
50 thin films of the viscous mixture to permit the rapid diffusion of the diol through the increasingly more viscous liquid. When the polyester reaches the desired viscosity, the polyester can be extruded, quenched and
55 chipped or extruded through spinnerettes or through a die for film-forming.

- A lighter polyester, such as a white polyester can be prepared by removing the unreacted diol from the hot direct esterification product. This can be done in the same reaction vessel through an attached side-arm condenser or in any separate vessel. It is desirable to keep the hot esterification product in an oxygen-free atmosphere while re-
65 moving water and unreacted diol.

The time required to prepare polyethylene terephthalate by the process according to the invention is substantially less than that required for its preparation by the ester-exchange method. The high pressure condensation generally requires about 60 minutes, while the low pressure polymerization is complete in approximately 2 to 3 hours. While the process according to the invention is particularly useful as a continuously conducted process, the process may be interrupted at any stage and continued later. The process is flexible. While the process involves a high pressure cycle and a low pressure cycle, the condensation and polymerization processes are not, necessarily, individually discrete, i.e. it is not necessary that one stage be complete before the next one is initiated.

Polymers prepared in accordance with the invention may be formed by conventional methods of spinning and casting into shaped articles such as films, tapes, fibres and bristles.

EXAMPLE 1

20.0 grams of terephthalic acid and 22.0 grams of ethylene glycol were charged into a stirred autoclave immersed in an oil bath exhibiting a temperature of 256°C. The autogenous pressure in the system was 50
95 psi and the atmosphere in the autoclave was nitrogen. The oil bath temperature was increased incrementally to 284°C over a period of 60 minutes. Substantially all water formed by the reaction and excess glycol were
100 allowed to distil out continuously under atmospheric pressure.

The glycol ester thus formed was polycondensed, after addition of 0.01 grams of antimony pentoxide to the autoclave, at
105 282°C and under a vacuum of approximately 0.10 millimetres of mercury during a reaction period of 150 minutes to give polyethylene terephthalate having an intrinsic viscosity of 0.74, and an ecru colour. The
110 fibre obtained from this polymer exhibited a good cold stretch.

EXAMPLE 2

The procedure of Example 1 was followed except that the temperature of the oil bath
115 during the condensation reaction was initially 258°C and was increased to 280°C. The polyethylene terephthalate fibre obtained exhibited an intrinsic viscosity of 0.70, an ecru colour after being ground, and good cold
120 stretch properties.

WHAT WE CLAIM IS:—

1. A process for preparing polyethylene terephthalate, which comprises forming a condensate by heating a mixture of tere-
125 phthalic acid and ethylene glycol to a temperature of at least 260°C under super-

- atmospheric pressure and thereafter polymerizing said condensate by heating it to a temperature of at least 260°C under atmospheric pressure in the presence of antimony pentoxide as a catalyst.
2. A process as claimed in claim 1, in which the catalyst is present during the initial condensation reaction and the reaction is carried out continuously.
3. A process as claimed in either of the preceding claims, wherein the molar ratio of ethylene glycol to terephthalic acid is within the range of 1:1 to 7:1.
4. A process as claimed in any preceding claim, in which the temperature is increased during the polymerization stage of the reaction.
5. A process as claimed in claim 1, substantially as described in either of the foregoing Examples.
6. Polyethylene terephthalate when prepared by the process claimed in any preceding claim.

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